Table 1: Preventative Maintenance Schedule and Parts List

Instrument	Items Checked/Serviced	Frequency	Critical Spare Parts
Atomic Absorption Spectrophotometer	Perform at least a 3-point calibration, and if readings are low, the operator checks the gas flows, burner, or cell alignment, wavelength slit width, photomultiplier voltage, and lamp intensity prior to analysis	Determined by analyst so that response and the calibration is within required specifications	Nebulizers, contact rings, graphite tubes, quartz windows
	Change graphite tubes and contact rings	Weekly, if needed as determined by analyst	
	Clean burner heads, nebulizers, quartz cells, and reduction flasks according to manufacturer instructions whenever excessive noise is apparent or whenever indicated by visual inspection	When color change is observed	
	Tygon tubing	6 months, or if deterioration is observed	
	Optical lenses	As needed	
Analytical Balance	Internal weight, train, gears, electronics	As needed, but at least annually	
Microscopes	Cleaned and serviced	As needed, but at least annually	

Table 1: Preventative Maintenance Schedule and Parts List (continued)

Instrument	Items Checked/Serviced	Frequency	Critical Spare Parts
Inductively Coupled Plasma Spectrophotometer	Sample introduction system (aspirator)	Daily, as needed	Torches, nebulizers, pump tubing, torch collars (bonnets)
	Check pumps and tubing	Weekly, as needed	Syringes, columns
	Clean nebulizer	As needed	
	Clean sample probe	Monthly	
	Check plumbing	Daily or as needed	
Ion Chromatograph	Check filter (inlet)	Weekly	None
	Flush column	After each new sample	
	Check bed support Clean cells	When specifications are off	
Infrared Spectrophotometer	Polystyrene Test Spectrum	Weekly	Chart paper, pens, set of 10 cm cells, set of 1 cm cells, source coils, ceramic rods
	Zero Adjustment	Weekly	
pH Meters	None	None	None
Ultraviolet (UV/VIS) Spectrophotometer	Lamp and wavelength check or serviced	As needed or during calibration steps of when used	Replacement cells
	Wash, rinse, and dry cells	Each use	

Table 1: Preventative Maintenance Schedule and Parts List (continued)

Instrument	Items Checked/Serviced	Frequency	Critical Spare Parts
GC/MS	Replace column, clean ion source, replace filaments	Determined by analyst so that response and the calibration are within required specifications	Septa Single taper injection port liners Ferrules Columns Syringes Filaments Toner Cartridges O-rings
	Check pump fluid and calibration gas vial	Weekly	
	Replace pump fluid	Every 6 months	
	Replace pump pellets	As needed	
	Check pump fluid		
	Printer maintenance	As needed	
	Clean instrument area	As needed	
	Autosampler maintenance (SVOA GC/MS systems only)	As needed	
		As needed	
	Change septum (SVOA GC/MS systems only)	As needed as determined by analyst	
	Injection port maintenance (SVOA GC/MS systems only)	As needed as determined by analyst	

Table 1: Preventative Maintenance Schedule and Parts List (continued)

Instrument	Items Checked/Serviced	Frequency	Critical Spare Parts
HPLC*	Detector lamps	If baseline is unstable or has excessive noise without flow through the cell	Pump seals Switching valve seals Check valve seals (inlet and outlet) Lamps Columns
	Pump seals, check valves, inlet frits	If HPLC system pressure becomes unstable while flow is isocratic	Tubing Ferrules/nuts
	Switching valve seals, injection volume metering device seals	If replicate injections are less than 95% of each other where chromatography is not in question	
Gas Chromatograph	Replace column or column packing, clean detector, clean or replace injection port liner.	Determined by analyst so that response and the calibration is within required specifications	Column ferrules Injection port liners and O-rings Autosampler syringes Deactivated glass wool Columns Column packings
	Replace septa	Weekly, if needed as determined by analyst	Injection port septa Detector ignitors PID Lamps Moisture traps
	Replace incoming gas drying cartridges	When color change is observed	Oxygen traps

**Flushing HPLC system:* After each use of a buffer of modifier, the HPLC system should be flushed with 20 milliliters water then 10 mL 50/50 (acetonitrile or methanol/water). The column may be included in this flushing if applicable.

**Water Mobile Phase:* Before each use of the HPLC system, the water last used must be replaced with fresh DI water in order to avoid bacteria that may have formed in the old water.

Repairs: All replacement of lamps, seals, or other parts should be performed according to the manufacturer's instructions.

STANDARD OPERATING PROCEDURE APPROVAL SHEET

SOP TITLE: Determination of Suspended Particulates in the Atmosphere Using Various Media

DOCUMENT CONTROL NUMBER: IH-002

EFFECTIVE DATE: February 16, 2018

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QUALITY ASSURANCE MANAGER Tracey Earle Date 2-16-18

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NEW	1	2	3	4	5	6
12/03	2/05	4/13	6/15	7/16	2/18	

STANDARD OPERATING PROCEDURE

DETERMINATION OF SUSPENDED PARTICULATES IN THE ATMOSPHERE USING VARIOUS MEDIA

1.0 SCOPE AND APPLICATION

1.1 This procedure provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter as specified in 40CFR 50 Appendices B and J.

1.2 The measurement process associated with this procedure is nondestructive and subsequent chemical analysis is possible, if required by the project.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of analytical balances. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 Filters used in this procedure are composed of glass fiber or other relatively inert, non-hygroscopic material. There are two filter sizes- 8 inches by 10 inches and 47 mm which are specified to have a minimum collection efficiency of 99 percent for 0.3 μm particles. The filter size is subject to change based on available field equipment.

1.5 The approximate concentration range applicable to this method is 2 to 750 $\mu g/m^3$ at standard conditions (25°C, 760 mm Hg).

1.5.1 The upper range is determined by the point at which the sampler can no longer maintain the specified flow rate due to the loading on the filter.

1.5.1.1 Filter loading and flow are affected by particle size distribution, moisture content of the particles collected, and filter variability among other things.

1.5.2 The lower range is determined by the sensitivity of the analytical balance and inherent sources of error.

2.0 SUMMARY OF METHOD

2.1 Filters are equilibrated for moisture, assigned an identifier and weighed prior to sampling.

2.2 Filters are then submitted to the client for sample collection. Sample collection occurs for a nominal 24-hour period and obtains a measured quantity of air.

2.3 When sampling has completed, the filters are returned to the laboratory where they undergo equilibration for moisture and are weighed.

2.4 If atmospheric conditions during sampling vary significantly from standard conditions, the concentration of the particulate should be corrected to reflect standard conditions.

3.0 SAFETY PRECAUTIONS

3.1 It is imperative that all laboratory personnel treat every sample as implicitly hazardous.

4.0 SAMPLE COLLECTION AND HANDLING

4.1 Samples should be taken in accordance with the sampling procedure found in 40 CFR50; however ALS does not participate in sampling activities.

4.2 Samples are inspected upon analysis for the following acceptance criteria. If these criteria are not met, it will be noted on the report.

4.2.1 Media will be inspected to ensure that correct filter was used for sampling

4.2.2 Filter condition- intact with no tears

4.2.3 Inspection for the presence of loose particulate

4.3 Careful handling of the filter between the pre-sampling and post-sampling weighing is necessary to avoid errors due to loss of fibers or particles from the filter.

4.4 The filter must not be folded prior to sampling as folding can create weakened areas within the filter and may cause errors or loss during sampling.

5.0 INSTRUMENTATION AND MATERIALS

5.1 Analytical balance with a sensitivity of 0.10 mg.

5.1.1 The current balance utilized for this procedure is a Mettler-Toledo 5-place analytical balance, but any equivalent balance may be utilized in accordance with this procedure.

5.2 Filter Conditioning Chamber: capable of maintaining the temperature between 15 °C and 30°C during equilibration and a controlled relative humidity of <50%.

5.3 Large Manila Envelopes: capable of enclosing an unfolded glass fiber filter (8 inches by 10 inches). Cassette holders in coin size manila envelopes are used for the 47 mm filters.

5.4 Balance weights- 0.01 (10mg), 1.0, and 3.0 grams (traceable to NIST).

6.0 PROCEDURE

6.1 The balance auto-calibration routine is performed and balances are verified before use with NIST traceable stainless steel weights - 0.01 gram for the 6 place balance and 1 gram for the 5 place balance.

6.1.1 TSP and PM_{10} filters that are 8X10 inches in size weigh approximately 4 grams. The 47 mm size filters weigh approximately 0.1 grams and can be used for $PM_{2.5}$ and PM_{10}. The range of verification encompasses the working range of use.

6.2 Pre-numbered Whatman glass microfiber filters are purchased from Fisher Scientific, but any equivalent filter or supplier is acceptable.

6.3 Filters are placed in the environmental chamber overnight for equilibration.

6.4 Filters are then weighed using the hanging balance capability of the Mettler-Toledo analytical balance.

6.5 Filters are placed in a manila envelope with a sheet of cardstock paper for support or in cassette holder within coin size manila envelope.

6.6 The High Volume Filter Identification Sheet is then attached to the front exterior of the manila envelope (see Appendix 9.1)

6.7 Filters are shipped to the client for sampling.

6.8 Filters returned from the client following sampling are logged in at the laboratory using the standard laboratory procedure.

6.9 Filters are removed from the envelopes by the analyst and replaced in the dessicator overnight for equilibration.

6.10 Following equilibration, filters are reweighed using step 6.3.

6.10.1 Weights are recorded in the designated TSP or PM_{10} filter electronic notebook.

6.10.2 Subtract the final weight from the initial filter weight to obtain the total concentration of the suspended particles.

7.0 QUALITY ASSURANCE PROVISIONS

7.1 A duplicate weight is completed at a frequency of at least every 10 samples.

7.2 Analytical balance performance must be verified prior to use using weights that have been verified by QA and are directly traceable to NIST calibrated weights.

7.3 Analytical balance performance is also ensured by external calibration service for an acceptable provider at least annually as required by laboratory procedure on supporting equipment, QA-011, current revision.

8.0 REPORTING RESULTS

8.1 Results are reported in mg/sample. If the client submits air volumes with the samples, results are reported in $\mu g/m^3$.

8.1.1 Microgram per cubic meter is calculated by:

$$\mu g / m^3 = \frac{A}{B} X\, 1000$$

where: A indicates sample concentration in mg/Sample
B indicates air volume sampled in standard meters^3

9.0 APPENDICES

9.1 High Volume Filter Identification Sheet Example

10.0 REFERENCES

10.1 40CFR50, Appendix B, "Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)," July 1, 1997, revised on July 1, 2014.

10.2 40CFR50, Appendix J, "Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere," July 1, 1997, revised on July 1, 2014.

10.3 40CFR50, Appendix L, "Reference Method for the Determination of Particulate Matter as PM2.5 in the Atmosphere," July 1, 1997, revised on July 1, 2014.

Appendix 9.1: High Volume Filter Identification Sheet Example

Hi-Vol. Data Record

Project:_____P.N.:_____

Station:_____

Site and/or Sample Number:_____

Sample Date:_____Filter No.:_____

Flow Reading: Initial_____Final_____Average_____

Running Time Meter: Initial_____Final_____

Total Sample Time:_____minutes

Total Air Volume:_____std m^3

Concentration:_____µg/std m^3

Optional:

Temperature: Initial_____Final_____Average_____

Barometric Pressure:
Initial_____Final_____Average_____

Comments:_____

Operator:_____

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DOCUMENT TITLE:	***METHODS IO-3.1 AND IO-3.4 MODIFIED FOR METALS PREPARATION AND ANALYSIS FOR SUSPENDED PARTICULATES***
REFERENCED METHOD:	*IO-3.1 AND IO-3.4*
SOP ID:	*IH-006*
REV. NUMBER:	*1*
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STANDARD OPERATING PROCEDURE APPROVAL SHEET

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4/13	2/18					

METHODS IO-3.1 AND IO-3.4 MODIFIED FOR METALS PREPARATION AND ANALYSIS FOR SUSPENDED PARTICULATES

1.0 SCOPE AND APPLICATION

1.1 This procedure describes the digestion and analysis of inorganic compounds for total suspended particulates (TSP) by ICP.

1.2 Table 1 lists compounds that are applicable to this modification of the preparation method detailed in the EPA Compendium Method IO-3.1.

1.2.1 Other elements may be prepared using this method if performance is demonstrated for the analytes of interest and at the concentration levels of interest. Performance may be demonstrated using spiked samples, acceptable linearity of calibration, and blank values that meet the requirements of the client or project.

TABLE 1: Elements applicable to this preparation and analysis method

Aluminum	Molybdenum
Arsenic	Sodium
Antimony	Silicon
Barium	Phosphorus
Beryllium	Platinum
Boron	Selenium
Cadmium	Silver
Calcium	Yttrium
Chromium	Tellurium
Cobalt	Thallium
Copper	Titanium
Iron	Tin
Lead	Tungsten
Nickel	Vanadium
Lithium	Zinc
Magnesium	Zirconium
Manganese	

1.3 The procedures found in this document are to be used by analysts trained in the preparation of samples, operation of an ICP, and the interpretation of resulting data. Inexperienced analysts should not attempt these procedures without the supervision of trained analysts.

2.0 SUMMARY OF THE METHOD

2.1 Total Suspended Particulate (TSP) media may be either on a filter roughly 8 inches by 10 inch in size or a filter 47mm in size. Media is specified to have a minimum collection efficiency of 99 percent for 0.3µm particles.

2.1.1 If sample is taken on 8 inches by 10 inch filter, take one-ninth (1/9) of the Total Suspended Particulate (TSP) sample is digested with a combination of 2 mL HNO_3 and 3 mL HCl for 1 hour at 95°C ± 5°C then adjusted to a final volume of 50 mL with Type II water. Digestates must be shaken vigorously immediately before filtering prior to analysis using the appropriate pore-sized Acrodisc attached to a disposable syringe to remove undigested media prior to analysis. If the sample is not shaken, results will be significantly lower than the actual value. Digestates are then analyzed using inductively coupled argon plasma atomic emission spectroscopy.

2.1.2 If sample is taken on a 47mm filter, the entire filter of the Total Suspended Particulate (TSP) sample is digested with a combination of 1 mL HNO_3 and 1 mL HCl for 1 hour at 95°C ± 5°C then adjusted to a final volume of 20 mL with Type II water. Digestates must be shaken vigorously immediately before filtering prior to analysis using the appropriate pore-sized Acrodisc attached to a disposable syringe to remove undigested media prior to analysis. If the sample is not shaken, results will be significantly lower than the actual value. Digestates are then analyzed using inductively coupled argon plasma atomic emission spectroscopy.

3.0 SAFETY PRECAUTIONS

3.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis.

3.2 Proper precautions such as the use of gloves, face shields, safety glasses, and lab coats are mandatory when dealing with these samples.

NOTE: Any gloves used must undergo prior testing to ensure that no method target compounds can be leached from the gloves when contacted by acid in liquid or vapor form.

4.0 SAMPLE HANDLING AND PRESERVATION

4.1 Filters used in this procedure are composed of glass fiber or other relatively inert, nonhygoscopic material.

4.2 The potential for cross-contamination of samples in the laboratory must be minimized during all stages of preparation and analysis.

4.2.1 Disposable plastic digestion vessels are used for routine preparation of samples to minimize the potential for cross-contamination of samples during sample preparation.

4.2.2 All glassware is washed with acid neutralizing soap, rinsed with DI water, and dried on a pegboard.

4.3 Plastic or glass containers may be used to store the samples. In the determination of trace metals, sample containers have the potential of introducing positive or negative errors in the measurement by (a) contributing contaminants through leaching or surface desorption, and (b) depleting analyte

concentrations through adsorption. Consequently, the collection and treatment of the samples prior to analysis requires particular attention.

5.0 SAMPLE PREPARATION

5.1 If Total Suspended Particulate (TSP) media is on a filter roughly 8 inches by 10 inch in size, cut a 1" x 8" strip from the 8 inch by 10 inch filter and transfer the sample to a clean digestion vessel. If Total Suspended Particulate (TSP) media is on a 47mm filter, place entire filter in to a clean digestion vessel.

5.2 Quality control samples for each batch of up to 20 samples of the same matrix are prepared as follows:

5.2.1 A reagent blank is prepared by adding the appropriate acids and water, if necessary, and completing the appropriate digestion technique. This sample verifies that the reagents are acceptable.

5.2.2 A media blank is prepared by cutting a 1 inch by 8 inch strip from a non-used TSP filter that is roughly 8 inches by 10 inch in size or by using a whole non-used 47mm filter. The media blank should be as similar to the client submitted sample as possible and contain all of the reagents, and at the same volumes, as used in the processing of the samples. The media blank must be carried through the entire sample digestion procedure at the same time that the samples are prepared.

5.2.3 A Laboratory Control Samples (LCS) is prepared by following the same steps as the blank in 5.2.2, but the technician must spike the blank media with the appropriate spiking solution(s). A Laboratory Control Sample Duplicate (LCSD) should also be prepared in the same manner as the LCS.

5.2.3.1 LCS/LCSD Spike amount of 0.5mL of appropriate spiking solution(s) is used for TSP samples sampled on a filter that is roughly 8 inches by 10 inch in size.

5.2.3.2 LCS/LCSD Spike amount of 0.2mL of appropriate spiking solution(s) is used for TSP sampled on a filter 47mm in size.

5.2.4 A Matrix Spike (MS) is prepared by randomly selecting a sample (unless it is specified by the client) and spiking the sample with the appropriate spiking solution(s) prior to the addition of any acid. A Matrix Spike Duplicate (MSD) should also be prepared in the same manner as the MS.

5.2.4.1 MS/MSD Spike amount of 0.5mL of appropriate spiking solution(s) is used for TSP samples sampled on a filter that is roughly 8 inches by 10 inch in size.

5.2.4.2 No MS/MSD is prepped on samples taken on filter 47mm in size.

5.3 Add appropriate concentrations of HNO_3 and HCL to each digestion vessel based on filter size.

5.3.1 Add 2 mL of concentrated HNO_3 and 3 mL of concentrated HCl to each digestion vessel for TSP samples taken on 8 inches by 10 inch filter.

5.3.2 Add 1 mL of concentrated HNO_3 and 1 mL of concentrated HCl to each digestion vessel for samples taken on 47mm filter.

5.4 Cover the digestion vessels with either a watch glass or a loosened screw-cap and place the digestion vessels on a heat source at a temperature of 95°C ± 5°C.

5.5 Allow the samples to reflux for 1 hour.

5.6 Remove the samples from the heat source and adjust to a final volume.

5.6.1 Final volume of 50mL for TSP samples taken on an 8 inch by 10 inch filter.

5.6.2 Final volume of 20mL for TSP samples taken on a 47mm filter.

5.7 Digestion vessels must be shaken vigorously immediately prior to filtering the digestate. If this step is not followed, the results will be significantly lower than the actual results and LCS/LCSD and MS/MSD recoveries may be outside of the acceptable limits.

5.8 Immediately following step 5.7, the digestate may be filtered using the appropriate pore size Acrodisc attached to a disposable syringe to remove suspended particulates prior to analysis.

6.0 REPORTING LIMITS

6.1 The standard reporting limits for routine matrices are listed in ELIMS.

6.2 These values must be adjusted if affected by the sample matrix or to take into account dilution of the sample.

6.3 The values may be adjusted to fulfill project requirements. Lower level reporting limits must be supported by a method detection limit study or reporting limit verification.

7.0 INTERFERENCES

7.1 Spectral interferences are the primary source of interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, inter-element correction factors and background correction.

7.2 The preparation and analytical systems must be monitored to assure freedom from contaminants. This is verified through the analysis of laboratory preparation blanks.

7.3 Glassware must be scrupulously cleaned and stored in a clean environment to prevent sample cross-contamination.

8.0 APPARATUS

8.1 Inductively coupled argon plasma emission spectrometer (Thermo Jarrell-Ash, Thermo iCAP, or equivalent):

8.1.1 Computer-controlled emission spectrometer with background correction.

8.1.2 Radio frequency generator.

8.1.3 ICP torch and load coil assembly.

8.1.4 Nebulizer and spray chamber.

8.1.5 Peristaltic pump.

8.1.6 Mass flow controller.

8.1.7 Autosampler

8.1.8 Water chiller (if necessary)

8.1.9 Drain assembly

8.1.10 Ventilation system

8.2 Argon gas supply - Welding grade or better.

8.3 Nitrogen gas supply - Welding grade or better.

8.4 Sample uptake tubing.

8.5 Variable and fixed volumetric pipettes. (10-1000µL, 1-10 mL)

8.6 Analytical balance capable of weighing 0.01 g.

8.7 Volumetric flasks (1 L).

8.8 Plastic screw top sample containers.

8.9 16mm x 125mm Plastic disposable culture tubes for Autosampler.

8.10 Digestion Vessels – appropriate for sample type and heat source.

8.11 Watch glasses.

8.12 Thermometer – capable of measuring the range of 0-200°C.

8.13 Filter apparatus – Appropriate pore-sized Acrodiscs attached to disposable syringes.

8.14 Heating source – Adjustable and able to maintain a temperature of 90-95°C (e.g. hotplate, hotblock, etc.).

9.0 REAGENTS AND STANDARDS

9.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

9.2 ASTM Type II Water [ASTM D1193-77 (1983)]. All references to water in the method refer to ASTM Type II unless otherwise specified.

9.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If the reagent blank is <MDL, the acid can be used.

9.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If the reagent blank is <MDL, the acid can be used.

9.5 Standard stock solutions may be purchased. ALS Cincinnati is currently purchasing High-Purity Standards certified 1000 ppm stock solutions. These standards are NIST traceable. The shelf-life of all stock solutions is one year from the day received. Alternatively, stock solutions may be prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

9.5.1 Calibration standard solutions are prepared by matching the acid combination and concentration in the samples.

9.5.2 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions with 50 mL of concentrated HNO_3 and 50 mL of concentrated HCL in 1000 mL volumetric flasks. Dilute to 1000 mL with Type II water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to check for possible spectral interferences and/or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging. New calibration standards must be initially verified against the initial calibration verification standard. Record all standard preparation information in the current working standards (WS) book.

Note: If the addition of silver results in an initial precipitation, warm the flask until the solution clears. Cool and dilute to 1000 mL with water.

10.0 CALIBRATIONS

NOTE: Inexperienced analysts should not attempt to operate ICP without the supervision of a trained analyst. Many components of the instrument, especially the sample introduction system and torch assembly, are easily damaged. Improper use of the instrument may result in very costly repairs and extended down-time.

10.1 The instrument performance should be optimized accordingly to the manufacturer's recommendations.

10.2 For routine analysis, initial calibration standards are prepared and analyzed at three levels (0, 1, and 10 ppm) although the number and concentrations of the standards may be changed to achieve project requirements, improve instrument performance, and/or to accommodate expected sample concentrations.

10.3 Following initial calibration, verify the instrument calibrations using ICV and ICB standards. Results obtained from the analysis of the ICV must be within +/- 20% of the true values for all analytes. If not, terminate the analysis, correct the problem, and recalibrate the instrument. The results of the ICB are to agree within three standards of deviation of the mean blank value. If not,

repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, and recalibrate.

10.4 The interference check samples (ICSA and ICSAB) contain known concentrations of interferents that will provide an adequate test of the correction factors. They are analyzed to verify the validity of the inter-element correction (IEC) factors. These solutions may be purchased, or prepared by spiking a blank with elements of interest, particularly those with know interferences at 0.5 to 1 mg/L. the acids content in these two solutions should be the same as in the calibration standards and samples.

10.4.1 The results obtained for all analytes in ISCA and ICSAB solutions should agree to within +/- 20% of the true value. If not, terminate the analysis, evaluate the data, and if deemed necessary, correct the problem, recalibrate the instrument, and reanalyze all samples since the last valid ICSA/ICSAB analysis.

10.4.2 If upon review of the data, it is determined that the interferences are not present in the samples. It is not necessary to repeat the analysis

10.5 The continuing calibration verification (CCV) check sample should be prepared in the same acid matrix as the calibration standards and samples with concentrations near the mid-range of calibration. The CCV may be prepped from the stock solutions used for the preparation of the calibration standards. This standard is analyzed after every 10 samples and at the end of the analytical sequence and should be within 20% of the true value for the analytes of interest. If not, terminate the analysis, evaluate the data, and if deemed necessary, determine the source of the variation, recalibrate the instrument and reanalyze all samples not bracketed by acceptable CCV results.

10.5.1 Certain results not bracketed by acceptable CCV results may provide acceptable results (i.e. positively-biased CCV's, but samples are non-detected for the analytes requested).

10.6 The continuing calibration verification (CCB) blank sample should be prepped in the same acid matrix as the calibration standards and samples. The CCB is analyzed after every CCV sample during the analytical sequence. The results of the CCB are to agree within three standard deviation of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, and recalibrate.

11.0 QUALITY ASSURANCE PROVISIONS

11.1 All quality control data must be maintained and readily available for reference and for auditing purposes.

11.2 Quality control provisions addressing initial and continuing calibration are found in section 10.0.

11.3 The preparation blank control limits and corrective actions are as follows:

Control limits: Less than the highest of either:
(1) The method detection limit,
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

Corrective Actions:

1) Check for calculation errors, instrument performance
2) Reanalyze blank and samples
3) Flag data

11.4 The results obtained for LCS and LCS duplicates must be within the laboratory specified control limits. If there is insufficient data to generate control limits (minimum 20 analyses), the results must be within +/- 20 % of the true value for LCS's. If any reported analytes fall outside of the control limits for the LCS or LCS duplicates, the data should be evaluated to determine if re-analysis is required. Certain results may be acceptable even with LCS/LCS Duplicate values that are beyond acceptable results (i.e. positively-biased LCS values, but samples are non-detected for the analytes of interest). If re-analysis is required, the problem must be corrected, and the associated samples must be re-analyzed for those analytes.

11.4.1 If, upon re-analysis, the LCS/LCS Duplicate values are still beyond laboratory specified limits, flag the resulting data as possibly possessing a bias.

11.4.2 Certain results not bracketed by acceptable CCV results may provide acceptable results (i.e. positively-biased CCVs, but samples are non-detected for the analytes requested).

11.5 The relative percent difference (RPD) of the LCS/LCS Duplicate analyses should be less than the laboratory established control limits. If there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of < 20% will be used. Flag all samples associated with the out of control duplicate results.

$$RPD = |[(D1-D2)/((D1 + D2)/2)] * 100|$$

where:

RPD = relative percent difference
D1 = first sample value
D2 = second sample value

11.6 An IDL study must be performed semi-annually, or every time the instrument is adjusted in a way which may affect the IDL's, whichever is more frequent. The IDL's are determined by first creating a standard which contains all of the analytes at concentrations between 3x and 5x the instrument manufacturer's suggested IDL's. This standard is then analyzed, under normal operating conditions, seven consecutive times per day, on three non-consecutive days. Each analysis must be performed in the same manner as typical analytical samples are measured, including rinsing between analyses with the reagent blank. The standard deviations obtained from the three sets of seven analyses, for each analyte, are averaged. The IDL's are obtained by multiplying by three the average of the three standard deviations for each analyte.

11.7 On a semi-annual basis, the linear range of each analyte must be established. This is accomplished by analyzing a linear range verification check standard during a routine analytical run,. The results obtained for all analytes must be within +/- 5 % of the true value. Otherwise, the problem must be corrected and the standard reanalyzed. The concentrations of each analyte in this check standard are the highest concentrations which can be reported in samples or QC standards. When results are obtained which exceed these values, the sample or QC standard must be diluted and reanalyzed.

11.8 Responsibility for inspection.

11.8.1 The Section Manager, or designee, is responsible for inspecting the work performed by the analysts to verify completeness, accuracy, and compliance to the referenced methods. The analysts are responsible for maintaining complete and detailed log books. The Section Manager or a peer analyst is responsible for reviewing, signing, and dating all completed logbook pages.

11.8.2 The analysts performing these procedures have the responsibility of inspecting the sample and digestate containers for damage and for proper sample labeling. Any non-conformance must be documented on an Analytical Non-conformance/Corrective Action form as described in the standard operating procedure for non-conformances. The Section Manager must be notified for further instructions and for client notification.

12.0 REPORTING RESULTS

12.1 Results should be reported in the units and format specified by the client or contract.

12.1.1 Results may be reported in µg/Sample or mg/Sample taken directly from the instrument quantitation list.

12.1.2 Results may also be reported in mg/m^3, provided that the client has supplied air volumes for each sample.

12.2 It is the responsibility of the Section Manager, or designee, to check the final report for transcription errors, proper rounding of numbers and correct number of significant figures, compliance with the method, and compliance with the requirements listed in this procedure.

12.3 All validated reports must be signed by the Project Manager.

13.0 REFERENCES

13.1 "Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Compendium Method IO-3.1 Selection, Preparation and Extraction of Filter Material,"(EPA/625/R-96/010a), Center of Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268, June 1999.

13.2 "Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Compendium Method IO-3.4 Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy," (EPA/625/R-96/010a), Center of Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268, June 1999.

13.3 40CFR50, Appendix B, "Reference Method for the Determination of Particulate Matter in the Atmosphere (High Volume Method)," July 1, 1997.

13.4 40CFR50, Appendix J, "Reference Method for the Determination of Particulate Matter as PM10 in the Atmosphere," July 1, 1997.

14.0 APPENDICES

14.1 None.

Not Controlled- please do not copy

STANDARD OPERATING PROCEDURE APPROVAL SHEET

SOP TITLE: Elements by ICP

DOCUMENT CONTROL NUMBER: IH-7300 modified

EFFECTIVE DATE: February 16, 2018

APPROVALS:

LAB DIRECTOR Joseph Riel Date 2-16-18

SECTION MANAGER Date 2-16-18

QUALITY ASSURANCE MGR. Tracey Earle Date 2-16-18

RECORD OF REVISIONS:

DATE	LOCATION OF REVISION	QA APPROVAL
2/16/18	QA review & no changes	Tracey Earle

RECORD OF REVISIONS:

NEW	1	2	3	4	5	6
11/00	3/14	1/15	4/15	4/16	2/18	

STANDARD OPERATING PROCEDURE
FOR
THE PREPARATION AND ANALYSIS OF ELEMENTS BY ICP

1.0 SCOPE AND APPLICATION

1.1 This procedure describes the digestion and analysis of air filter samples for elements by ICP.

1.2 Table 1 lists compounds that are applicable to this modification of the preparation method detailed in NIOSH method 7300.

TABLE 1: Elements applicable to this preparation and analysis method

Aluminum	Molybdenum
Arsenic	Sodium
Antimony	Silicon
Barium	Phosphorus
Beryllium	Platinum
Boron	Selenium
Cadmium	Silver
Calcium	Yttrium
Chromium	Tellurium
Cobalt	Thallium
Copper	Titanium
Iron	Tin
Lead	Tungsten
Nickel	Vanadium
Lithium	Zinc
Magnesium	Zirconium
Manganese	

1.3 The procedures found in this document are to be used by analysts trained in the preparation of samples, operation of ICPs, and the interpretation of resulting data. Inexperienced analysts should not attempt these procedures without the supervision of trained analysts.

2.0 SAFETY PRECAUTIONS

2.1 ALS Environmental, Cincinnati has a current Radiological License through the Ohio Department of Health. In order to limit exposure to personnel, radiological and/or beryllium containing samples are segregated from non-regulated material at the time of login. All radiological samples are stored in a locked, controlled storage cabinet. Only trained personnel may receive, handle, prepare, store, and dispose of regulated samples as stated in SOPs RAD-003, RAD-004, and RAD-005. Any questions on the handling of radiological samples should be directed to the current RSO.

2.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health

hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis.

2.3 Proper PPE such as the use of safety glasses, lab coats, and gloves are mandatory during the preparation and analysis of samples.

2.3.1 Additional personal protection may be used when deemed necessary.

NOTE: Any gloves used must undergo prior testing to ensure that no method target compounds can be leached from the gloves when contacted by acid in liquid or vapor form.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Samples are most commonly collected on mixed cellulose ester (MCE) filters, polyvinylchloride (PVC) filters, but other media types may be acceptable.

3.2 The potential for cross contamination in the laboratory must be minimized during all stages of preparation and analysis.

3.2.1 Disposable plastic digestion vessels are used for routine preparation of samples to minimize the potential for cross contamination of samples during sample preparation.

3.2.2 All glassware is washed with a non-phosphate detergent in hot water and rinsed with tap water. The glassware is then soaked in an acid (1:1 HNO_3) bath and rinsed with tap water. Finally, the glassware is soaked in another acid (1:1 HCl) bath, rinsed with tap water and deionized water then hung upside down to dry on a pegboard. After air-drying, all glassware is stored in cabinets to minimize contamination due to airborne particulate. Immediately prior to use, the glassware is rinsed with Type II water.

3.3 Plastic or glass containers may be used to store the samples. In the determination of trace metals, sample containers have the potential of introducing positive or negative errors in the measurement by (a) contributing contaminants through leaching or surface desorption, and (b) depleting analyte concentrations through adsorption. Consequently, the collection and treatment of the samples prior to analysis requires particular attention.

4.0 REPORTING LIMITS

4.1 The standard reporting limits for each analyte are located in LIMS.

4.1.1 The reporting limits are subject to change based on client requests and/or project requirements.

4.1.2 If the sample requires a dilution, the reporting limit will be raised to reflect the dilution.

5.0 INTERFERENCES

5.1 Spectral interferences are the primary source of interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction.

5.1.1 Determine the location for off-line background correction by scanning the interference check solution (aluminum, calcium, iron and magnesium at a minimum concentration of 100ppm. Additional elements may be added) and comparing the scan to the wavelength of interest. Refer to the instrument manufacturer's instruction for application of the background correction point. The background correction point corrects for background shift and not interelement spectral interference. Background correction must be determined by an experienced analyst.

5.1.2 Determine the interelement correction (IEC) factors by analyzing single source interfering element standards (aluminum, calcium, iron and magnesium at a minimum of 100 ppm, additional elements may be added). Background correction must be applied prior to determination of IECs. Measure the apparent concentration of analyte of interest resulting from the analysis of the interfering element. Refer to the instrument manufacturer's instruction for application of the interelement correction factor. This should be performed on a semi-annual basis.

5.2 Compensate for physical interferences (high dissolved solids, varying viscosity) by using a high solids nebulizer, diluting sample and/or varying of the instrument sample introduction and plasma parameters. All modifications to the instrument must be performed by an experienced analyst.

5.3 Glassware must be scrupulously cleaned and stored in a clean environment to prevent sample cross-contamination.

5.4 Matrix match all standards and samples when possible.

5.5 The preparation and analytical systems must be monitored to assure freedom from contaminants. This is verified through the analysis of laboratory reagent and media blanks.

6.0 APPARATUS

6.1 Inductively coupled argon plasma emission spectrometer.

6.1.1 Computer-controlled emission spectrometer with background correction

6.1.2 Radio frequency generator

6.1.3 ICP torch and load coil assembly

6.1.4 Nebulizer and spray chamber

6.1.5 Peristaltic pump

6.1.6 Mass flow controller

6.1.7 Autosampler

6.1.8 Water chiller (if necessary)

6.1.9 Drain assembly

6.1.10 Ventilation system

6.1.11 Argon gas supply - Welding grade or better

6.1.12 Sample uptake tubing

6.2 Variable and fixed volumetric pipettes (10-1000µL, 1-10mL)

6.3 Analytical balance capable of weighing 0.01g

6.4 Volumetric flasks (1L)

6.5 Plastic screw top sample containers

6.6 Plastic disposable culture tubes for the Autosampler

6.7 Digestion vessels appropriate for sample type and heat source

6.8 Thermometer capable of measuring the range of 0-200°C

6.9 Appropriate pore-sized Acrodiscs (Nylon and Teflon) attached to disposable syringes

6.10 Hotblock or equivalent, adjustable and able to maintain a temperature of 90-95°C

7.0 REAGENTS

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 ASTM Type II Water. All references to water in the method refer to ASTM Type II unless otherwise specified. If method blank is <MDL, the water can be used.

7.3 Nitric Acid (HNO_3), concentrated. Acid should be analyzed to determine levels of impurities. If method blank is <MDL, the acid can be used.

7.4 Hydrochloric Acid (HCl), concentrated. Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

7.5 Intermediate standard solutions may be purchased. ALS, Cincinnati is currently purchasing High-Purity Standards certified stock solutions. These standards are NIST traceable and are provided with an expiration date by the manufacturer.

7.5.1 Alternatively, stock solutions may be prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

7.6 All calibration standards and instrument QC samples should be prepared by matching the acid combination and concentration in the samples.

7.7 Calibration standards: Prepare the standard by pipetting the indicated volume of intermediate standard into approximately 750mL of water that has been acidified with 50mL of HNO_3 and 50mL of HCl. Dilute the standard to a final volume of 1L and mix thoroughly. This list may be modified to accommodate fewer or additional elements.

7.7.1 To prepare a calibration standard at 10ppm:

Analyte	Concentration (mg/L)	Volume of Analyte (mL)	Final Volume (mL)	Final Concentration (mg/L)
[1] Mix A	1000	10.0	1000	10.0
[2] Mix B	1000	10.0	1000	10.0
[3] Mix C	1000	10.0	1000	10.0
Gallium	1000	10.0	1000	10.0
Indium	1000	10.0	1000	10.0
Platinum	1000	10.0	1000	10.0

[1] Mix A: purchased mixed standard containing Al, As, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, P, K, Na
[2] Mix B: purchased mixed standard containing Sb, Bi, Mo, Si, Te, Sn, Ti, W, Zr
[3] Mix C: purchased mixed standard containing Ba, Be, Li, Mn, Ni, Se, Sr, Tl, V, Y, Zn

7.7.2 To prepare a calibration standard at 1ppm:

Analyte	Concentration (mg/L)	Volume of Analyte (mL)	Final Volume (mL)	Final Concentration (mg/L)
[1] Mix A	1000	1.0	1000.	1.0
[2] Mix B	1000	1.0	1000.	1.0
[3] Mix C	1000	1.0	1000.	1.0
Silver	1000	1.0	1000.	1.0

[1] Mix A: purchased mixed standard containing Al, As, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, P, K, Na
[2] Mix B: purchased mixed standard containing Sb, Bi, Mo, Si, Te, Sn, Ti, W, Zr
[3] Mix C: purchased mixed standard containing Ba, Be, Li, Mn, Ni, Se, Sr, Tl, V, Y, Zn

7.7.3 If the addition of Silver results in an initial precipitation, warm the flask until the solution clears. Cool and dilute to 1000mL with reagent water.

7.8 Initial Calibration Verification (ICV) / Continuing Calibration Verification (CCV): Prepare the standard by pipetting the indicated volume of intermediate standard into approximately 750mL of water that has been acidified with 50 mL of HNO_3 and 50mL of HCl. Dilute the standard to a final volume of 1L and mix thoroughly. This mix will yield a solution containing Al, As, Ba, Cd, Ca, Cr, Ga, In, Fe, Pb, Mg, Pt, K, Se and Na at

5ppm. The mix also yields a solution containing Sb, Be, B, Bi, Co, Cu, Li, Mn Mo, Ni, P, Si, Sr, Te, Tl, Sn, Ti, V, W, Zn and Zr at 0.5ppm. This list may be modified to accommodate fewer or additional elements.

7.8.1 Any intermediate standard used to prepare the ICV/CCV solution must come from a different lot number than the intermediate standard used to prepare the calibration standards.

7.8.2 To prepare an ICV/CCV solution:

Analyte	Concentration (mg/L)	Volume of Analyte (mL)	Final Volume (mL)
[1] Mix A	1000	5.0	1000
[2] Mix B	1000	5.0	1000
[3] Mix C	100	1.0	1000
Silver	1000	1.0	1000
Gallium	1000	5.0	1000
Indium	1000	5.0	1000
Platinum	1000	5.0	1000

[1] Mix A: purchased mixed standard containing Al, As, Ba, Cd, Ca, Cr, Fe, Pb, Mg, K, Se, Na
2 Mix B: purchased mixed standard containing Sb, Bi, Mo, Si, Te, Sn, Ti, W, Zr
3 Mix C: purchased mixed standard containing Be, B, Co, Cu, Li, Mn, Ni, P, Sr, Tl, V, Y, Zn

7.8.3 If the addition of Silver results in an initial precipitation, warm the flask until the solution clears. Cool and dilute to 1000mL with reagent water.

7.9 Lowcheck: Prepare the standard by pipetting the indicated volume of intermediate standard into approximately 750mL of water that has been acidified with 50 mL of HNO_3 and 50mL of HCl. Dilute the standard to a final volume of 1L and mix thoroughly. This mix will yield a solution containing As, Sb, Ba, Be, B, Bi, Cd, Co, Cr, Cu, Li, Pb, Mn, Mo, Ni, P, Si, Se Sr, Te, Tl, Sn, Ti, V, W, Zn, and Zr at 20ppb. The mix will yield a solution containing Ga and In at 100ppb and Pt at 250ppb. This list may be modified to accommodate fewer or additional elements.

7.9.1 Any intermediate standard used to prepare the Lowcheck solution should come from a different lot number than the intermediate standard used to prepare the calibration standards.

7.9.2 To prepare a Lowcheck solution:

Analyte	Concentration (mg/L)	Volume of Analyte (mL)	Final Volume (mL)	Final Concentration (mg/L)
[1] Mix A	1000	0.02	1000	0.02
[2] Mix B	1000	0.02	1000	0.02
[3] Mix C	100	0.2	1000	0.02
Silver	1000	0.02	1000	0.02
Gallium	1000	0.1	1000	0.1
Indium	1000	0.1	1000	0.1
Platinum	1000	0.25	1000	0.25

1 Mix A: purchased mixed standard containing Al, As, Ba, Cd, Ca, Cr, Fe, Pb, Mg, K, Se, Na
2 Mix B: purchased mixed standard containing Sb, Bi, Mo, Si, Te, Sn, Ti, W, Zr
3 Mix C: purchased mixed standard containing Be, B, Co, Cu, Li, Mn, Ni, P, Sr, Tl, V, Y, Zn

7.9.3 If the addition of Silver results in an initial precipitation, warm the flask until the solution clears. Cool and dilute to 1000mL with reagent water.

7.10 The Blank (0ppm Calibration Standard), the Initial Calibration Blank (ICB), and the Continuing Calibration Blank (CCB) are prepared by adding acids to reagent water to achieve a final concentration of 5% HCl and 5% HNO_3 by volume.

7.11 Interference Check Solution A: Prepare the standard by pipetting 50mL of the ICSA intermediate standard into approximately 750mL of water that has been acidified with 50 mL of HNO_3 and 50mL of HCl. Dilute the standard to a final volume of 1L and mix thoroughly. The ICSA intermediate standard is purchased at concentrations of 5000ppm for Al, Ca, and Mg and 2000ppm for Fe.

7.12 Interference Check Solution AB: Prepare the standard by pipetting 50mL of the ICSA intermediate standard and 10mL of the ICSAB intermediate standard into approximately 750mL of water that has been acidified with 50mL of HNO_3 and 50mL of HCl. Dilute the standard to a final volume of 1L and mix thoroughly. The ICSAB working standard is purchased at concentrations of 50ppm for Ba, Be, Cr, Co, Cu, Mn, and V and 100ppm for Cd, Pb, Ni, Ag, and Zn.

7.13 New calibration standards must be initially verified against the ICV.

7.14 The analyte concentrations and acid amounts may be varied to accommodate non routine analyses or to achieve specific project goals.

7.15 More or less than 1L of each standard may be prepared. All acid and intermediate standard volumes must be adjusted according to the desired final volume.

7.16 Freshly mixed standards should be prepared as needed with the realization that concentration can change as the solution ages.

7.17 All prepared standards expire one year from the date of preparation unless otherwise specified.

7.18 All standards preparation information must be recorded in the current working standards logbook.

8.0 CALIBRATIONS

NOTE: Inexperienced analysts should not attempt to operate the ICP without the supervision of a trained analyst. Many components of the instrument, especially the sample introduction system and torch assembly, are easily damaged. Improper use of the instrument may result in very costly repairs and extended down-time.

8.1 The instrument performance should be optimized according to the manufacturer's recommendations.

8.2 For routine analyses, initial calibration standards are analyzed at two levels (0 and 10ppm or 0 and 1ppm) although the number and concentrations of the standards may be changed to achieve project requirements, improve instrument performance, and/or to accommodate expected sample concentrations.

8.3 Following initial calibration, verify the instrument calibrations using the ICV and ICB standards.

8.3.1 Results obtained from the analysis of the ICV must be within +/- 10% of the true values for all analytes of interest. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.3.2 The results of the ICB are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, and recalibrate.

8.4 Verify the instrument's capability to produce accurate results at low concentrations. The lowcheck concentration of an analyte should be less than or equal to the reporting limit. If the reporting limit of an analyte is less than the lowcheck concentration, properly dilute the lowcheck to achieve a concentration lower than that of the reporting limit when possible. The results obtained from the analysis of the lowcheck should be within +/- 20% of the true value for all analytes of interest. If not, the analyst should terminate the analysis, correct the problem, and re-calibrate the instrument.

8.5 The interference check samples (ICSA and ICSAB) contain known concentrations of interferents that will provide an adequate test of the correction factors. They are analyzed to verify the validity of the inter-element correction (IEC) factors. These solutions may be purchased, or prepared by spiking a blank with the elements of interest, particularly those with known interferences at 0.5 to 1mg/L. The acid content in these two solutions should be the same as in the calibration standards and samples.

8.5.1 The results obtained for all analytes in ICSAB should agree to within +/- 20% of the true value. If not, terminate the analysis, evaluate the data, and, if deemed necessary, correct the problem, recalibrate the instrument, and reanalyze all samples since the last valid ICSAB analysis.

8.5.2 If, upon review of the data, it is determined that the interferents are not present in the samples, then it is not necessary to repeat the analysis.

8.6 The continuing calibration verification (CCV) check sample should be prepared in the same acid matrix as the calibration standards and samples with concentrations near the mid-range of calibration. This standard is analyzed after every 10 samples and at the end of the analytical sequence and should be within 10% of the true value for the analytes of interest. If not, terminate the analysis, evaluate the data, and, if deemed necessary, determine the source of the variation, re-calibrate the instrument and re-analyze all samples not bracketed by acceptable CCV results.

8.6.1 Certain results not bracketed by acceptable CCV results may provide acceptable results (i.e. positively-biased CCVs, but samples are non-detected for the analytes requested).

8.7 The continuing calibration verification (CCB) blank sample should be prepared in the same acid matrix as the calibration standards and samples. The CCB is analyzed after

every CCV sample during the analytical sequence. The results of the CCB are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, and recalibrate.

8.7.1 Certain results not bracketed by acceptable CCB results may provide acceptable results (i.e. positively-biased CCBs, but samples are non-detected for the analytes requested).

9.0 SAMPLE PREPARATION

9.1 Thoroughly clean the workspace that is to be used with DI water and dry. Place an appropriate sized piece of absorbent liner or equivalent over the workspace to help aid in the minimization of any potential cross contamination.

9.2 Using a pair of clean tweezers, place a blank filter into a labeled digestion vessel to serve as a Media Blank (MBLK) as well as two more blank filters into two separate, labeled digestion vessels to serve as a Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD).

9.2.1 The blank media is purchased by an approved vendor and should matrix match the field samples. It should be noted if the blank media does not matrix match the field samples.

9.3 Carefully open the cassette that is housing the sample and using a pair of tweezers, transfer the filter to a clean, properly labeled digestion vessel.

9.3.1 The tweezers must be cleaned in between samples to aid in the minimization of any potential cross contamination.

9.3.2 To ensure any loose particulate left in the cassette is quantitatively transferred to the digestion vessel, the cassette may be rinsed with a known amount of 10% acid, adding the rinsate to the digestion vessel.

9.2.2.1 The amount of rinsate added to the digestion vessel must be taken into consideration when adjusting the final volume of the digestate.

9.3.3 A Reagent Blank (RB) must be prepared for each analytical batch of twenty or fewer field samples. The reagent blank must contain all the reagents at the same volumes as used in the processing of the samples and it must be carried through the entire sample digestion procedure at the same time that the samples are prepared.

9.3.4 A MBLK must be prepared for each analytical batch of twenty or fewer field samples. The MBLK must be matrix matched when possible, and it must include all of the reagents at the same volumes as used in the processing of the field samples. The MBLK must be carried through the entire sample digestion procedure at the same time that the samples are prepared.

9.3.5 Prepare a LCS and LCSD per analytical batch of twenty or fewer field samples. The LCS pair is prepared by spiking blank media (matrix matched when possible) with known concentrations of the analytes of interest. The LCS and LCSD must also include all of the reagents at the same volumes as used in the

processing of the field samples, and they must be carried through the entire sample digestion procedure at the same time that the field samples are prepared.

9.3.5.1 Add the proper aliquot of each spiking solution to the digestion vessel prior to the addition of any acid. The target for the spike should be 1ppm with the exception of Potassium, whose target spike should be 10ppm.

9.3.5.1.1 Example: If a 100ppm spiking solution is used, and the final volume of the sample is 20mL, add 0.2mL of each spiking solution to the digestion vessel.

9.3.5.2 Should the client request the analysis of an analyte that is not included in the designated spiking solution mix, then a single source standard may be used. Again, the target for the spike should be 1ppm and should be spiked accordingly.

9.3.5.3 Target spikes for LCS/LCSD samples may change to better suit client's needs, element recovery, or project requirements.

9.3.6 A reporting limit verification sample must be prepared for each batch of AIHA-ELLAP samples prepared. This sample consists of a blank matrix that matches the matrix of the client samples when possible. The blank matrix is then spiked with a single source standard at the level that corresponds to the matrix appropriate reporting limit.

9.3.6.1 Only one reporting limit verification sample is required per matrix per day.

9.3.7 Additional QC samples may be prepared and analyzed upon client request.

9.4 Add 0.8mL of concentrated HNO_3 and 1.2mL of concentrated HCl to each digestion vessel.

9.5 Cover the digestion vessels with a loosened screw cap and place the vessels on a hotblock set at 90-95°C.

9.6 Allow the samples to reflux for 1 hour.

9.7 Samples submitted for the analysis of Beryllium only are to be prepared by adding 2.0mL of concentrated HNO_3 and placed on a hotblock at a temperature of 90-95°C for 2 hours.

9.8 Remove the samples from the hotblock, and after the samples are allowed to cool, adjust to a final volume of 20mL.

9.9 Tightly cap and shake to mix the contents of the digestion vessel.

9.10 Digestates must be filtered using the appropriate pore size Acrodisc attached to a disposable syringe to remove suspended particulates prior to analysis and must be filtered into an appropriate sized plastic disposable culture tube. The samples are now ready for analysis.

9.10.1 Nylon filters should be used unless the client is requesting the analysis of Antimony, Gold, and/or Thallium in which a Teflon filter should be used to ensure maximum analyte recovery.

10.0 DIAGRAMS OR TABLES

10.1 None

11.0 PROCEDURE

11.1 Fill the rinse reservoir.

11.2 Connect pump winding and insert the sample probe into distilled water.

11.3 Follow the manufacturer's instructions for instrument start-up and plasma ignition. A default setting is provided by the manufacturer and must not be modified unless instructed by the manufacturer.

11.4 Allow the plasma to equilibrate for one hour. An equilibration time of less than an hour may result in drift.

11.5 If applicable, perform an alignment/profile. This function is both hardware and software dependent. Refer to the manufacturer's instructions for guidance.

11.6 Standards and samples may be analyzed manually or using an autosampler.

11.6.1 The autosampler is controlled through the instrument software. Refer to the manufacturer's instruction. The instrument software controls the calibration, QC checks and sample analysis automatically.

11.6.2 Perform manual analysis by inserting the probe into each sample. Acquire the reading using the instrument operating software. Care must be taken to assure sufficient rinse time between samples to prevent carryover.

11.7 Perform the analysis in this order: Calibration, ICV, ICB, Lowcheck, ICSA, ICSAB, a maximum of 10 samples, CCV, CCB. Repeat the analysis of a maximum of ten samples followed by a CCV, CCB as necessary. Upon completion of all sample analysis, an ICSA, ICSAB, CCV and CCB must be analyzed.

11.7.1 The ICSA and ICSAB may be run more frequently following a CCV/CCB to act as closing QCs should there be any QC failures later in the run. If failures occur, the samples that are not bracketed with passing QCs will need to be re-analyzed, not the entire sequence.

12.0 CALCULATIONS

12.1 Follow the instrument manufacturer's instructions for data entry of the sample to obtain the desired units. Derive the concentration from a total of 3 exposures per reading. Examples of proper dilution correction and unit conversion are shown below.

12.2 Sample Concentration (ug/sample) = [(µg/mL) From Instrument] * [Final Volume (mL)]

12.2.1 If a dilution was required for the sample, the sample concentration and reporting limit must both be multiplied by the dilution factor.

12.3 Percent recovery calculation for LCS and LCSD:

$$\text{Percent Recovery} = 100 * \frac{Measured\ Value}{Target\ Value}$$

12.4 Precision calculation for LCS and LCSD:

$$\text{Relative Percent difference (RPD)} = 100 * \frac{|V_1 - V_2|}{(V_1 + V_2)/2}$$

Where:

V_1, V_2 = found concentrations

13.0 QUALITY ASSURANCE PROVISIONS

13.1 All quality control data must be maintained and readily available for reference and for auditing purposes.

13.2 Quality control provisions addressing initial and continuing calibration are found in the Calibrations section of this SOP.

13.3 The Media Blank control limits and corrective actions are as follows:

Control limits: Less than the highest of either:
(1) The method detection limit,
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

Corrective Actions:
1) Check for calculation errors, instrument performance
2) Reanalyze blank and samples if possible
3) Flag data if necessary

13.4 The results obtained for the LCS and LCSD must be within the current control limits listed in LIMS. Control limits are subject to change without notice and are revised according to laboratory standard operating procedure. If there is insufficient data to generate control limits (minimum 20 analyses), the results should be within +/- 20% of the true value. If any reported analytes fall outside of the control limits for the LCS or LCSD, the data should be evaluated to determine if re-analysis is required. Certain results may be acceptable even with LCS/LCSD values that are beyond acceptable results (i.e. positively-biased LCS values, but samples are non-detected for the analytes of interest). If re-analysis is required, the problem must be corrected, and the associated samples must be re-analyzed for those analytes.

13.4.1 If, upon re-analysis, the LCS/LCSD values are still beyond laboratory specified limits, flag the resulting data as possibly possessing a bias.

13.5 The relative percent difference (RPD) of the LCS/LCSD analyses should be less than the laboratory established control limits located in LIMS. Control limits are subject to change without notice and are revised according to laboratory standard operating procedure. If

there is insufficient data to generate control limits (minimum 20 analyses), advisory limits of <20% may be used. Flag all samples associated with the out of control duplicate results.

13.6 A method detection limit (MDL) study must be performed annually, or every time the instrument is adjusted in a way which may affect the MDLs, whichever is more frequent. Refer to the current laboratory procedure for MDLs.

13.7 An IDL study is performed semi-annually, or every time the instrument is adjusted in a way which may affect the IDL, whichever is more frequent. The IDL is determined by first creating a standard which contains all of the analytes at concentrations between 3x and 5x the instrument manufacturers' suggested IDL. This standard is then analyzed, under normal operating conditions, seven consecutive times per day, on three non-consecutive days. Each analysis must be performed in the same manner as typical analytical samples are measured, including rinsing between analyses with the reagent blank. The standard deviations obtained from the three sets of seven analyses, for each analyte, are averaged. The IDL is obtained by multiplying by three the average of the three standard deviations for each analyte.

13.8 On a semi-annual basis, the linear range of each analyte is established. This is accomplished by analyzing a linear range verification check standard during a routine analytical run. The results obtained for all analytes must be within +/- 10% of the true value. Otherwise, the problem must be corrected and the standard reanalyzed. The concentrations of each analyte in this check standard are the highest concentrations which can be reported in samples or QC standards. When results are obtained which exceed these values, the sample or QC standard must be diluted and reanalyzed.

14.0 REPORTING RESULTS

14.1 Results should be reported in the units and format specified by the client or contract.

14.1.1 Results may be reported in µg/sample or mg/sample taken directly from the instrument quantitation list.

14.1.2 Results may also be reported in mg/m^3, provided that the client has supplied air volumes for each sample.

14.2 All validated reports must be signed by the reviewer.

15.0 PREVENTITIVE MAINTENANCE

15.1 Follow the manufacturer's recommendations for preventative maintenance of the instruments.

16.0 REFERENCES

16.1 "Elements by ICP: Method 7300," NIOSH Manual of Analytical Methods, Fourth Edition, Issue 2, August 15, 1994.

17.0 APPENDICES

17.1 None.

DOCUMENT TITLE:	SUPPORTING EQUIPMENT CALIBRATIONS AND VERIFICATIONS
SOP ID:	QA-011
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STANDARD OPERATING PROCEDURE APPROVAL SHEET

SOP TITLE: Supporting Equipment Calibrations and Verifications

DOCUMENT CONTROL NUMBER: QA-011

EFFECTIVE DATE: March 2, 2018

APPROVALS:

LAB DIRECTOR _____ Date 3/2/18

QUALITY ASSURANCE MANAGER Tracey Earle Date 3-2-18

RECORD OF MINOR REVISIONS:

DATE	LOCATION OF REVISION	QAU APPROVAL
3/2/18	Sec. 3.2	Tracey Earle

RECORD OF MAJOR REVISIONS:

NEW	1	2	3	4	5	6
10/03	11/05	10/13	4/15	8/15	9/16	3/17
7	8	9	10	11	12	13
3/18						

STANDARD OPERATING PROCEDURE

SUPPORTING EQUIPMENT CALIBRATIONS AND VERIFICATIONS

1.0 PURPOSE

1.1 This procedure provides guidance on the activities that ensure that the equipment that supports analytical activities is capable of intended use and assure that data generated using this equipment will meet client requirements and traceability requirements.

2.0 SCOPE AND AREA OF APPLICATION

2.1 This procedure applies to general laboratory equipment that directly supports analytical processes and does not apply to computers, software, or specific analytical instrumentation that is addressed in determinative laboratory procedures.

3.0 RESPONSIBILITIES

3.1 The Laboratory Director is ultimately responsible for all activities including quality assurance and control within the laboratory.

3.2 The QA/QC Manager, or designee, has the responsibility of monitoring supporting equipment, such as refrigerators, balances, weights, pipettes, microscopes, the Hotblock digestion system, reagent water polisher and thermometers to ensure that they are performing accurately, reliably and are calibrated to meet the criteria for use. Any reference equipment that needs to be sent out of the lab for calibration or repair will be packaged according to manufacturer's recommendations to ensure safe handling and transport.

3.2.1 Documentation of these verifications is maintained by QA/QC.

3.3 Analysts and technicians have the responsibility to ensure that the equipment used is properly functioning and has been properly verified prior to use.

3.4 For equipment that must be verified prior to use, analysts and technicians have the responsibility of performing and documenting these verifications in either their notebooks or logbooks assigned to the equipment.

4.0 REFERENCES

4.1 ISO/IEC 17025 (current version), General Requirements for the Competence of Testing and Calibration Laboratories.

4.2 AIHA Laboratory Accreditation Policies, LLC (current version)

4.3 NIST HANDBOOK 150, Procedures and General Requirements

4.4 ASTM D1193-99, Standard Specification for Reagent Water

4.5 EPA Method 9050A, Revision 1, December 1996.

4.6 The NELAC Institute (TNI) Standard Version 2009, July 1, 2011.

5.0 PROCEDURAL REQUIREMENTS

5.1 See Procedure Section.

6.0 PROCEDURAL DETAILS

6.1 Monitoring refrigerators and freezers to ensure that sample temperature requirements are met.

6.1.1 The storage refrigerators and freezers will be monitored during each work day by QA/QC or a designee.

6.1.2 At the beginning of each month, a monthly calendar will be taped to the refrigerator/freezer for which it will apply.

6.1.3 The calendar will reflect the refrigerator/freezer identification, the thermometer identifier, the control limits for the temperature, and the month and year for which the calendar applies.

6.1.3.1 The refrigerator/freezer identification used can be the ALS identification number, the refrigerator/freezer's manufacturer's serial number or other unique identifier.

6.1.3.2 The thermometer identification used will be the manufacturer's serial number.

6.1.3.3 The absolute control limits for refrigerators are 4 ± 2 °C and for freezers are -10 to -20 °C.

6.1.4 Each work day, QA/QC, or designee, will document the temperature of the unit by reading the thermometer at eye level and writing the temperature value and the initials of the individual responsible for making the observation, in the calendar square corresponding to the correct date.

6.1.4.1 QA/QC must take appropriate action for any deviations outside of the absolute control limits.

6.1.4.2 Samples must be removed from any refrigerator/freezer that is not functioning adequately and placed into another properly functioning unit.

6.1.4.3 In the event that the temperature is below the low control limit, adjust the temperature control to a warmer setting to return the temperature to the required level and allow sufficient time for temperature stabilization (approx. 2-4 hours) then verify the temperature to ensure that it meets the required criteria.

6.1.4.4 In the event that the temperature is above the high control, adjust the temperature control to a cooler setting to return the temperature to the required level and allow sufficient time for temperature stabilization (~2-4 hours) then verify the temperature to ensure that it meets the required criteria.

6.1.4.5 If the initial adjustments do not return the temperature to the required level, make further adjustments following the same procedure and allowing the same stabilization time before the temperature is re-verified.

6.1.4.6 If adjustments are not possible or if the adjustments do not return the unit to the required temperature, obtain service from a qualified external service or replace the unit.

6.1.4.7 The malfunctioning unit will be tagged during adjustments and service to ensure that analysts do not inadvertently utilize a unit that does not perform to required specification.

6.1.4.8 Any maintenance performed on the unit must be documented on the temperature monitoring calendar.

6.1.5 The calendars are replaced at the end of each month and the completed calendars are archived by QA/QC as quality records.

6.2 Monitoring laboratory balances

6.2.1 Balances are monitored across the expected range of use prior to the first use of the day by the analyst/technician using weights that are assigned by QA/QC to each balance.

6.2.1.1 Tare the balance and ensure that the reading is 0.

6.2.1.2 Place one of the assigned weights on the balance making sure not to touch the surface of the weight as oils and dust from contact with skin can lead to a faulty reading and/or calibration.

6.2.1.3 Record the reading in the balance logbook.

6.2.1.4 Remove the weight and return it to its protective storage container.

6.2.1.5 Repeat steps 6.2.1.2 through 6.2.1.4 for all weights across the expected range of use.

6.2.1.6 Acceptable performance ranges for balances can be found in the individual balance logbooks.

6.2.1.6.1 If the balance fails to meet the required criteria and is capable of internal recalibration, the analyst should activate the internal calibration program and upon completion of the calibration routine, re-verify the acceptable balance performance.

6.2.1.6.2 If following internal recalibration or if internal calibration is not possible, contact QA/QC immediately for further instruction and assistance.

6.2.1.7 The weight verification and the initials and date of verification are documented in the logbook assigned to the balance by QA/QC.

6.2.1.7.1 If internal recalibration has been performed, document the recalibration in the balance logbook.

6.2.1.8 When the logbook is filled, return it to QA/QC for archive as quality records.

6.2.1.9 The weights assigned to each balance will be verified at least annually by an external calibration service with a NIST/NVLAP calibration service. See section 6.3.

6.2.1.9.1 The verification of balance weights will be documented in a QA/QC notebook and the boxes containing the weights will be labeled to notify laboratory personnel of the verified status.

6.2.2 At least weekly, the balance calibrations are verified by QA/QC, or designee, across the expected range of use using the NIST traceable weight sets for each balance.

6.2.2.1 Verify the weights as in 6.2.1.1 through 6.2.1.5 using the NIST traceable weight set.

6.2.2.2 Acceptable performance limits for all balances are listed in the individual balance logbooks.

6.2.2.3 The documentation of this verification is maintained in a QA/QC notebook assigned to weekly checks.

6.2.3 Balances and the NIST traceable weight sets are verified at least annually by an external calibration/repair service that performs calibration, and any service necessary, on-site.

6.2.3.1 The current service provider for the balances is Brechbuhler Scales Incorporated, 9914 Crescent Park Dr., Cincinnati, OH 45069 (Phone: 513-777-5800). Mettler Toledo is the service provider for the Mettler Toledo analytical balances (1900 Polaris Parkway Columbus, OH 43240 phone: (800) METTLER).

6.2.3.2 An equivalent service provider may be used as long as they maintain NVLAP or ISO/IEC 17025 (current version) certification and can issue a certificate that contains the required information.

6.2.3.2.1 Information required on calibration certificates for all balances include: appropriate statements of measurement results, measurement uncertainty, and traceability.

6.3 Monitoring balance weights and calibration verification.

6.3.1 At least annually, the NIST traceable lab weight sets are sent to a calibration service for verification or a new set of NIST traceable weights are purchased from a qualified calibration service.

6.3.1.1 The current balance weight calibration provider is Troemner Precision Weights and Calibration Services, 201 Wolf Drive, P.O. Box 87, Thorofare, NJ 08086-0087 (Phone: 856-686-1600).

6.3.1.2 An equivalent service provider may be used as long as they maintain NVLAP or ISO/IEC 17025 (current version) certification.

6.3.1.3 Information required on calibration certificates for all weights include: appropriate statements of measurement results, measurement uncertainty, and traceability.

6.3.2 Weights must be re-calibrated or newly purchased to at least the level of ASTM Level 1 and the service provider must supply a NVLAP type certification for each weight that specifically documents the associated uncertainty with each weight.

6.3.3 Upon receipt of the weights from the calibration service, the associated documentation is archived by QA/QC as quality records.

6.3.4 QA/QC then performs the annual verification of the weights assigned to each balance in the laboratory.

6.3.4.1 Using the 5-digit analytical balance, tare the balance and then weigh verify the calibration using the newly calibrated NIST traceable balance weights.

6.3.4.1.1 Each reading should be within the acceptable performance range listed in the individual balance logbooks.

6.3.4.2 Record the weight as the reference value in the QA/QC notebook.

6.3.4.3 Return the NIST weight to its protective storage container and select a balance assigned weight to be verified.

6.3.4.4 Place the balance weight on the analytical balance pan and record the weight in the QA/QC notebook.

6.3.4.5 For the weight to be acceptable for daily use, the reading should be within ± 1 graduation of the target weight.

6.3.4.6 Weights that are beyond the required specification must be replaced or recalibrated by an acceptable calibration laboratory. See 6.3.1.1.

6.3.4.7 Weights that are determined to be acceptable during the verification process are returned to their protective cases and the cases are labeled with the re-verification information.

6.3.4.8 Verified weights are then returned to the assigned analytical balance.